Colloidal ferric oxide: a new photosensitizer for grafting acrylamide onto cellulose acetate films

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(Received 11 November 1992)

The photografting of acrylamide onto cellulose acetate films using light of wavelength >380 nm is discussed. The semiconducting properties of colloidal Fe_2O_3 (bandgap 2.2 eV) is used for photosensitizing the reaction. Degree of grafting is dependent upon the concentration of the photosensitizer as well as that of the monomer. Methyl viologen (MV^{2+}) is used to prevent e^-–h^+ recombination.

(Keywords: photografting; cellulose acetate; acrylamide; Fe_2O_3; MV^{2+})

Introduction

Polymers play an important role in modern society. Attempts are being made to modify their properties in the solid state by grafting vinyl monomers onto the polymers; various methods are being used, such as radiation-induced grafting, photografting, etc.[1]. When a cellulosic material absorbs light of wavelength <340 nm it undergoes photodegradation, creating active sites on its polymer backbone to which vinyl monomers may be grafted[2]. Photografting may also be initiated by absorption of light of wavelength >340 nm by using a photosensitizer, e.g. benzoin ethyl ether (BEE)[3], sodium 2,7-anthraquinone disulfonate, benzophenone[4], etc. The mechanism for photosensitization is the same for all these photosensitizers, i.e. they undergo photodegradation creating radicals which abstract hydrogen atoms from the base polymer, thus creating active sites onto which the vinyl monomer is grafted.

This paper discusses the use of colloidal Fe_2O_3 as a photosensitizer, which absorbs photons of bandgap energy, promoting the electrons to the conduction band. The valence band holes can abstract hydrogen atoms from the cellulose acetate film, thus creating active sites onto which acrylamide may be grafted. Thus, by using the semiconducting properties of colloidal Fe_2O_3 (bandgap 2.2 eV), photografting by near-u.v.–visible light has been made possible. Methyl viologen (MV^{2+}) is used as an electron scavenger to prevent e^-–h^+ recombination:

$$\alpha\text{-}Fe_2O_3 \xrightarrow{h\nu} h^+ + e^-$$

$$e^- + MV^{2+} \rightarrow MV^+$$

$$h^+ + \text{cell–H} \rightarrow \text{cell}^\bullet$$

$$\text{cell}^\bullet + M \rightarrow \text{cell–M}^\bullet$$

where M = acrylamide.

Experimental

Cellulose acetate films (~ 0.05 mm thick) were prepared by slow evaporation from acetone solution. The films were cut into small pieces (1 cm × 1 cm) and were cleaned thoroughly with benzene by Soxhlet distillation before use. Acrylamide (BDH) was recrystallized three times from acetone and dried under vacuum before use. Colloidal Fe_2O_3 was prepared with particle size >60 nm and used as such[5]. Methyl viologen (MV^{2+}, Fluka) was used as received.

A known weight of cellulose acetate film (vacuum dried) was placed in a Pyrex glass cell containing aqueous solutions of colloidal Fe_2O_3, MV^{2+} (10^{-3} M) and acrylamide (1 M). The total volume of the solution was 20 cm^3. The solution was degassed for 1 h by argon gas. The film was then irradiated with a 450 W xenon lamp fitted with i.r. cut-off filter and 380 nm low-pass filter. The irradiated film was taken out, washed thoroughly with double-distilled water to remove the polyacrylamide gel adhering to the film surface, and then vacuum dried. The film was weighed and degree of grafting was measured as:

$$\text{Degree of grafting (\%)} = \frac{\text{wt of grafted film} - \text{wt of original film}}{\text{wt of original film}} \times 100$$

Preirradiation. Cellulose acetate film of known weight was placed in a Pyrex glass cell containing 20 cm^3 deaerated colloidal Fe_2O_3 solution (1 mg), and irradiated with a 450 W xenon lamp for 24 h. The film was taken out and placed in a Pyrex glass cell containing 20 cm^3 deaerated acrylamide solution (0.5 M), degassed for 20 min and heated at 50°C in a waterbath for 5 h. The film was then taken out, washed, vacuum dried and weighed to measure the degree of grafting.

Scanning electron microscopy. SEM pictures of the grafted and ungrafted films were taken in a Hitachi 600 SEM (magnification 2000 ×).

Results and discussion

Figure 1 shows the SEM pictures of the grafted and ungrafted cellulose acetate films. *Figure 1a* is the micrograph of the ungrafted film, *Figures 1b* and *1c* are micrographs of acrylamide grafted films using Fe_2O_3 as photosensitizer in simultaneous and preirradiation

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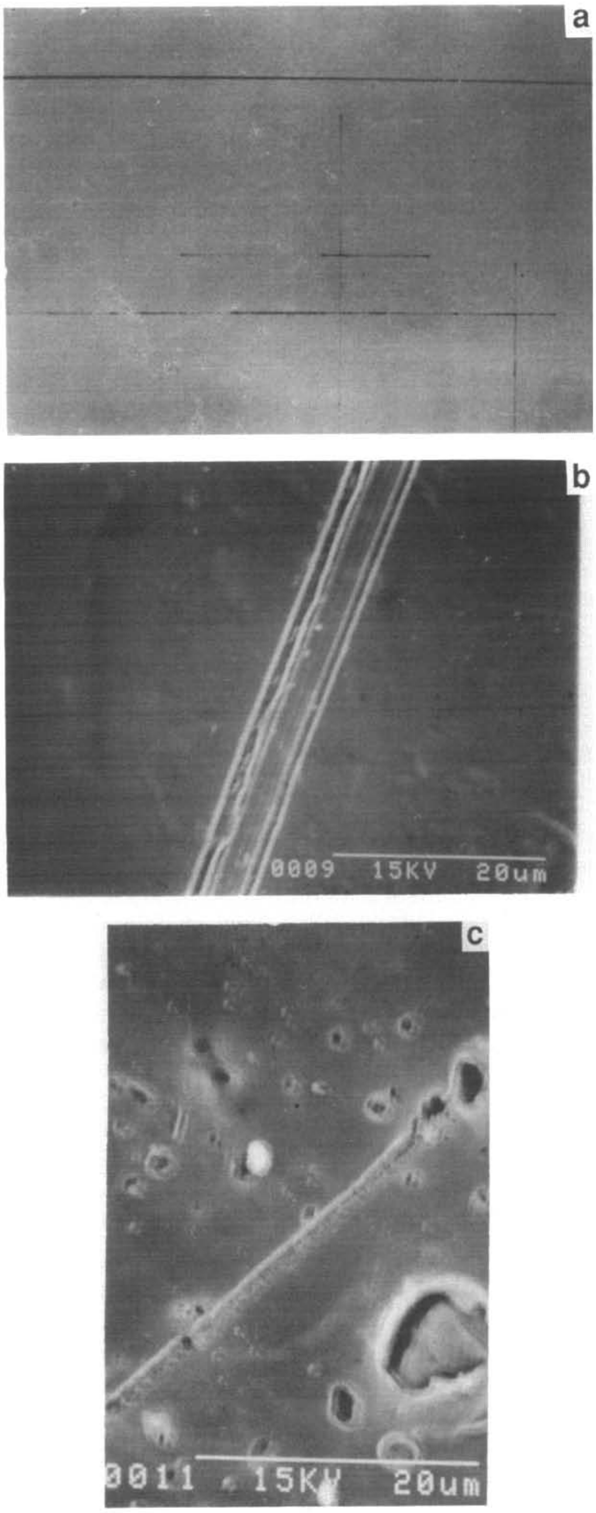

Figure 1 Scanning electron micrographs of ungrafted and grafted cellulose acetate films. (a) Ungrafted film; (b) acrylamide grafted film with simultaneous irradiation; (c) acrylamide grafted film with preirradiation process (magnification 2000×)

Table 1 Relationship between degree of grafting and acrylamide concentration at constant $[Fe_2O_3]$ of 1.35 mg per 20 cm^3 of solution

[Acrylamide] (M)	Degree of grafting (%)
0.25	8.66
0.5	9.70
1.00	10.31
1.25	16.35

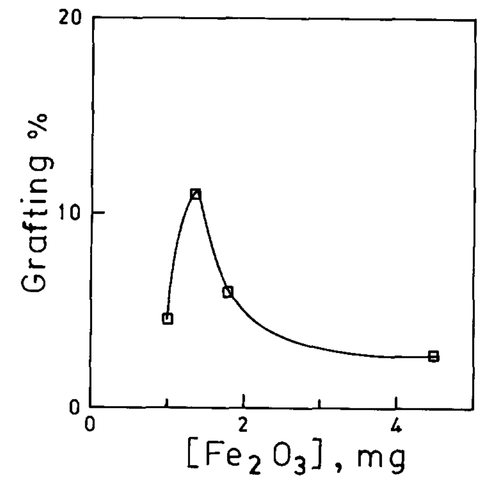

Figure 2 Variation of degree of grafting with concentration of colloidal Fe_2O_3. ([acrylamide] = 1 M)

grafting processes, respectively. From these pictures it is evident that grafting has taken place using Fe_2O_3 as photosensitizer. The role of Fe_2O_3 as photosensitizer is evident from *Figure 1c*, i.e. grafting by preirradiation, where no acrylamide was present during irradiation. That cellulose acetate itself may undergo photodegradation is unacceptable because it is already known[2] that cellulose undergoes photodegradation at <340 nm. Also, blank experiments without Fe_2O_3 did not result in grafting.

Figure 2 shows the variation in degree of grafting at different concentrations of Fe_2O_3. The degree of grafting increases with increasing concentration of Fe_2O_3 up to a maximum point and then decreases with higher concentrations of the sensitizer, probably due to scattering of light by the large number of Fe_2O_3 particles. The maximum degree of grafting is at $[Fe_2O_3] \cong 1.35$ mg per 20 cm^3 of solution.

Table 1 gives the relationship between degree of grafting and acrylamide concentration at constant $[Fe_2O_3]$. It is seen that the degree of grafting increases with increase of monomer concentration up to 1.25 M, as has been observed by Yan *et al.*[6], who, however, showed that beyond a certain monomer concentration the degree of grafting decreases. We did not observe such a decrease in the degree of grafting in the range of monomer concentration from 0.25 M to 1.25 M. Further increase in the monomer concentration was not possible because of the difficulty in removing the polyacrylamide gel adhering to the film surface.

Conclusion

Grafting of acrylamide onto cellulose acetate films may be accomplished by using colloidal Fe_2O_3 as the photosensitizing agent at wavelength >380 nm.

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